

Liquid Crystalline Schiff Bases Containing a 2,5-bis-(*p*-aminophenyl)-[1,3,4]oxadiazole Bent Core

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*The synthesis and liquid crystalline properties of some new Schiff bases based on a [1,3,4]oxadiazole core are reported. Compounds were prepared by condensation reaction of 2,5-bis-(*p*-aminophenyl)-[1,3,4]oxadiazole (1) with mesogenic groups containing azo linkage based on 4-(4-alkoxyphenylazo)-benzaldehyde (2a÷2f) and 4-(4-alkanoyloxyphenylazo)-benzaldehyde (3a÷3g). All the reported compounds present liquid crystalline properties, evidenced by DSC and POM analysis.*

Keywords: Schiff bases, [1,3,4]oxadiazole, liquid crystals, azo compounds

Banana-shaped molecules are the result of a systematic research for new molecular shapes compatible with liquid crystalline properties. Since it has been shown that ferroelectricity is possible in such liquid crystalline materials composed of achiral molecules, the bent or "banana-shaped" liquid crystals have turned into a major field of research [1].

The results obtained by different research groups gave evidence that the molecular structure- mesomorphic properties relationships are much more complicated than that for rod-liquid crystals and, at the moment, are not well understood. Nevertheless, it is now obvious that the liquid crystalline properties are very sensitive against any molecular change in these bent molecules [2].

Most banana-shaped liquid crystals, reported up to now, contain an appropriate central core unit to which two symmetric or asymmetric wings are connected [3-7].

The compounds synthesized in this work are based on a 2,5-bis-(*p*-aminophenyl)-[1,3,4]oxadiazole core (1) and contain azo and imino linking groups between the phenylene units (scheme 1). The presence of azo group may undergo *trans-cis* isomerization under UV irradiation, making these materials photoresponsive.

All the reported compounds present liquid crystalline properties under polarized optical microscopy (POM) and DSC investigations.

Experimental part

Materials and methods

All materials were used as purchased unless mentioned otherwise. 2,5-Bis-(*p*-aminophenyl)-[1,3,4]oxadiazole (1) was obtained using literature data [8]. Synthesis of compounds 2a ÷ 2f and 3a ÷ 3g was previously reported [9].

All melting points were determined using a Linkam heating stage and Linksys 32 temperature control unite in conjunction with a Axioscop 40 Zeiss polarizing optical microscope and Qimaging/Retiga - 4000R camera for image capture, the transitions being confirmed by DSC analysis (Mettler Toledo TGA-SDTA 851e). Heating and cooling cycles were run at rates of 10°C/min under nitrogen atmosphere, with samples measured in closed lid aluminum pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase

standards. The thermal analysis was performed on 4 ÷ 5 mg/samples on a Mettler-Toledo TGA SDTA851e derivatograph in N₂ atmosphere, with a flow rate of 20 mL/min, with a heating rate of 10 K/min from 25 to 900°C. FT-IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrometer (NaCl crystal window). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was carried out on a PerSeptive Biosystems-Voyager-DE (Framingham, MA) mass spectrometer operating in linear mode. The spectrometer equipped with a nitrogen laser (337 nm) was calibrated using Angiotensin II and Bombesin as standards. The laser steps and voltages applied were adjusted as a function of the molecular weight and the nature of the compound. The matrix used in MALDI-TOF mass spectrometry was 2,5-dihydroxybenzoic acid. The solvent used for both matrix and sample was tetrahydrofuran (THF). A typical procedure used for sample preparation was as follows. The matrix (10 mg) was dissolved in 1 mL of THF. The sample concentration was 2-5 mg/mL. The matrix solution (25 mL) and the sample solution (5 mL) were mixed well, and then 0.5 mL of the resulting solution was loaded into the MALDI-plate and dried before inserting into the vacuum chamber of the MALDI machine. Elemental analysis was performed on Fisons EA1108 CHN.

Synthesis

2,5-Bis-(*p*-aminophenyl)-[1,3,4]-oxadiazole (1) has been prepared by the reaction of *p*-aminobenzoic acid with hydrazine sulphate in polyphosphoric acid (PPA), according to a published method [8].

4-(4-alkoxyphenylazo)-benzaldehyde (2a ÷ 2g) and 4-(4-alkanoyloxyphenylazo)-benzaldehyde (3a÷3f) have been prepared by Williamson etherification and esterification reactions [9].

General procedure for the preparation of Schiff bases

The iminic compounds were obtained by condensation reactions of 2,5-bis-(*p*-aminophenyl)-[1,3,4]oxadiazole (1) with the appropriate aldehydes in anhydrous ethanol in the presence of a catalytic amounts of glacial acetic acid. Reflux time: 48 h. The precipitated products were filtered out while hot and washed with ethanol. The products were purified by recrystallization from DMSO, $\eta = 43 \div 71\%$.

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2,5-bis-(4-hexyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (4a)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-hexyloxyphenylazo)-benzaldehyde (2a) (0.49 g, 1.58 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 53\%$ (0.35 g), m.p. (liquid crystal): 113°C (K₁/K₂), 254°C (LC₂/LC₃), 326°C (LC₃/D), 310°C (I/LC₁), 237°C (LC₂/K₂). FT-IR (KBr, cm⁻¹): 2934, 2860 (ν_{C-H}), 1601 (ν_{C=N}), 1250, 843, 559. Anal. Calcd for C₅₉H₅₂N₈O₃: C 74.62, H 6.26, N 13.39, found C 74.65, H 6.24, N 13.31. m/z: 837.31 [M+1]⁺.

2,5-bis-(4-heptyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (4b)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-heptyloxyphenylazo)-benzaldehyde (2b) (0.51 g, 1.58 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 61\%$ (0.42 g), m.p. (liquid crystal): 135°C (K₁/K₂), 203°C (K₁/K₂), 239°C (LC₂/LC₃), 327°C (LC₃/D), 315 (I/LC₁), 289°C (LC₂/LC₃), 208°C (LC₂/K₂). FT-IR (KBr, cm⁻¹): 2924, 2855 (ν_{C-H}), 1599 (ν_{C=N}), 1252, 845, 559. Anal. Calcd for C₆₁H₅₆N₈O₃: C 74.97, H 6.52, N 12.95, found C 74.94, H 6.54, N 12.92. m/z: 865.38 [M+1]⁺.

2,5-bis-(4-octyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (4c)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-octyloxyphenylazo)-benzaldehyde (2c) (0.54 g, 1.60 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 71\%$ (0.5 g), m.p. (liquid crystal): 127°C (K₁/K₂), 205°C (K₁/K₂), 229°C (LC₂/LC₃), 330°C (LC₃/D), 318 (I/LC₁), 305°C (LC₂/LC₃), 193°C (LC₂/K₂). FT-IR (KBr, cm⁻¹): 2922, 2855 (ν_{C-H}), 1601 (ν_{C=N}), 1252, 845, 559. Anal. Calcd for C₆₃H₆₀N₈O₃: C 75.31, H 6.77, N 12.55, found C 75.33, H 6.74, N 12.58. m/z: 892.89 [M+1]⁺.

2,5-bis-(4-nonyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (4d)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-nonyloxyphenylazo)-benzaldehyde (2d) (0.56 g, 1.59 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 43\%$ (0.3 g), m.p. (liquid crystal): 138°C (K₁/K₂), 183°C (K₁/K₂), 219°C (LC₂/LC₃), 322°C (LC₃/D), 312 (I/LC₁), 258°C (LC₂/LC₃), 176°C (LC₂/K₂). FT-IR (KBr, cm⁻¹): 2920, 2853 (ν_{C-H}), 1601 (ν_{C=N}), 1252, 847, 559. Anal. Calcd for C₆₅H₆₄N₈O₃: C 75.62, H 7.00, N 12.16, found C 75.59, H 7.03, N 12.14. m/z: 921.29 [M+1]⁺.

2,5-bis-(4-decyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (4e)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-decyloxyphenylazo)-benzaldehyde (2e) (0.58 g, 1.58 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 60\%$ (0.45 g), m.p. (liquid crystal): 138°C (K₁/K₂), 184°C (K₁/LC₂), 215°C (LC₂/LC₃), 321°C (LC₃/D), 309 (I/LC₁), 289°C (LC₂/LC₃), 180°C (LC₂/K₂). FT-IR (KBr, cm⁻¹): 2920, 2851 (ν_{C-H}), 1601 (ν_{C=N}), 1250, 845, 559. Anal. Calcd for C₆₇H₆₈N₈O₃: C 75.92, H 7.22, N 11.80, found C 75.90, H 7.25, N 11.82. m/z: 948.75 [M+1]⁺.

2,5-bis-(4-octadecyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (4f)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-octadecyloxyphenylazo)-benzaldehyde (2f) (0.76 g, 1.59 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 44\%$ (0.4 g), m.p. (liquid crystal): 175°C (K₁/LC₂), 187°C (LC₂/LC₃), 280°C (LC₃/D), 275°C (I/LC₁), 171°C (LC₂/K₂), 150°C (K₁/K₂). FT-IR (KBr, cm⁻¹): 2918, 2849 (ν_{C-H}), 1601 (ν_{C=N}),

1254, 845, 559. Anal. Calcd for C₇₆H₁₀₀N₈O₃: C 77.77, H 8.59, N 9.55, found C 77.80, H 8.57, N 9.52. m/z: 1173.17 [M+1]⁺.

2,5-bis-(4-pentanyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (5a)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-pentanyloxyphenylazo)-benzaldehyde (3a) (0.49 g, 1.58 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 45\%$ (0.30 g), m.p. (liquid crystal): 228°C (K₁/K₂), 244°C (K₂/LC₂), 264°C (LC₂/LC₃), 333°C (LC₃/D). FT-IR (KBr, cm⁻¹): 2957, 2930, 2870 (ν_{C-H}), 1753 (ν_{C=O}), 1589 (ν_{C=N}), 856, 559. Anal. Calcd for C₃₀H₄₄N₈O₅: C 71.75, H 5.30, N 13.39, found C 71.77, H 5.33, N 13.37. m/z: 837.53 [M+1]⁺.

2,5-bis-(4-hexanyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (5b)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-hexanyloxyphenylazo)-benzaldehyde (3b) (0.51 g, 1.57 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 44\%$ (0.30 g), m.p. (liquid crystal): 214°C (K₁/K₂), 232°C (K₁/LC₂), 342°C (LC₂/D). FT-IR (KBr, cm⁻¹): 2928, 2868 (ν_{C-H}), 1753 (ν_{C=O}), 1591 (ν_{C=N}), 856, 561. Anal. Calcd for C₃₂H₄₈N₈O₅: C 72.20, H 5.59, N 12.95, found C 72.18, H 5.61, N 12.97. m/z: 865.19 [M+1]⁺.

2,5-bis-(4-heptanyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (5c)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-heptanyloxyphenylazo)-benzaldehyde (3c) (0.54 g, 1.60 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 31\%$ (0.22 g), m.p. (liquid crystal): 80°C (K₁/K₂), 134°C (K₁/LC₂), 253°C (LC₂/D). FT-IR (KBr, cm⁻¹): 2928, 2855 (ν_{C-H}), 1753 (ν_{C=O}), 1605 (ν_{C=N}), 856, 561. Anal. Calcd for C₃₄H₅₂N₈O₅: C 72.63, H 5.87, N 12.55, found C 72.65, H 5.90, N 12.52. m/z: 893.46 [M+1]⁺.

2,5-bis-(4-octanyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (5d)

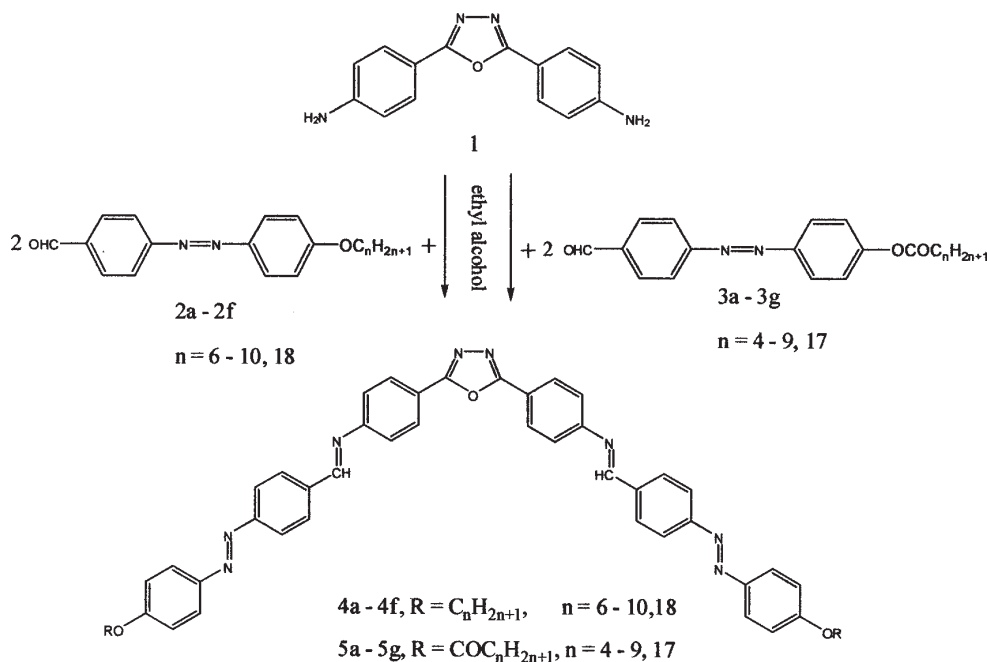
Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-octanyloxyphenylazo)-benzaldehyde (3d) (0.56 g, 1.59 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 55\%$ (0.4 g), m.p. (liquid crystal): 64°C (K₁/K₂), 174°C (K₁/LC₂), 219°C (LC₂/LC₃), 343°C (LC₃/D). FT-IR (KBr, cm⁻¹): 2924, 2853 (ν_{C-H}), 1753 (ν_{C=O}), 1589 (ν_{C=N}), 856, 561. Anal. Calcd for C₃₆H₅₆N₈O₅: C 73.02, H 6.13, N 12.17, found C 73.04, H 6.10, N 12.20. m/z: 921.47 [M+1]⁺.

2,5-bis-(4-nonyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (5e)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-nonyloxyphenylazo)-benzaldehyde (3e) (0.58 g, 1.58 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 33\%$ (0.25 g), m.p. (liquid crystal): 193°C (K₁/K₂), 204°C (K₁/LC₂), 249°C (LC₂/LC₃), 321°C (LC₃/D). FT-IR (KBr, cm⁻¹): 2920, 2851 (ν_{C-H}), 1753 (ν_{C=O}), 1589 (ν_{C=N}), 854, 559. Anal. Calcd for C₃₈H₆₀N₈O₅: C 73.39, H 6.37, N 11.81, found C 73.41, H 6.35, N 11.84. m/z: 948.76 [M+1]⁺.

2,5-bis-(4-decanoyloxyphenylazo-4-phenylmethylimino-4-phenyl)-[1,3,4]oxadiazole (5f)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (1) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-decanoyloxyphenylazo)-benzaldehyde (3f) (0.60 g, 1.58 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 45\%$ (0.35 g), m.p. (liquid crystal): 192°C (K₁/K₂), 204°C (K₁/LC₂), 234°C (LC₂/LC₃), 332°C (LC₃/D). FT-IR (KBr, cm⁻¹): 2918, 2849 (ν_{C-H}), 1753 (ν_{C=O}), 1589 (ν_{C=N}), 854, 559. Anal. Calcd for



Scheme 1. Synthesis of Schiff bases based on a [1,3,4]oxadiazole core

$\text{C}_{60-64}\text{H}_{18}\text{N}_8\text{O}_5$: C 73.75, H 6.60, N 11.47, found C 73.72, H 6.62, N 11.50. m/z : 977.22 $[\text{M}+1]^+$.

2,5-bis-(4-octadecanoyloxyphenylazo)-4-phenylmethylimino-4-phenyl-[1,3,4]oxadiazole (5g)

Quantities: 2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole (**1**) (0.2 g, 0.79 mmol) in 15 mL ethanol, 4-(4-octadecanoyloxyphenylazo)-benzaldehyde (**3g**) (0.78 g, 1.58 mmol) in 15 mL ethanol, glacial acetic acid (1-2 drops), $\eta = 32\%$ (0.30 g), m.p. (liquid crystal): 96°C (K/K_s), 194°C (K_s/LC_1), 335°C (LC_3/D). FT-IR (KBr, cm^{-1}): 2918, 2849 ($\nu_{\text{C-H}}$), 1751 ($\nu_{>\text{C}=\text{O}}$), 1589 ($\nu_{>\text{C}=\text{N}}$), 854, 559. Anal. Calcd for $\text{C}_{76}\text{H}_{96}\text{N}_8\text{O}_5$: C 75.96, H 8.05, N 9.33, found C 75.93, H 8.08, N 9.31. m/z : 1201.61 $[\text{M}+1]^+$.

Results and discussion

Synthesis of Schiff bases

The Schiff bases were prepared by using the synthetic route presented in scheme 1. Synthesis of compounds **4a-f** and **5a-g** involved the condensation reaction of the core compound **1** with mesogenic groups containing azo linkage based on 4-(4-alkoxyphenylazo)-benzaldehyde (**2a-f**) and 4-(4-alkanoyloxyphenylazo)-benzaldehyde (**3a-g**) in ethanol, with yields between 31 ÷ 71 %.

The structural characterization of these compounds was established by using elemental analysis, FT-IR (no -CH=O absorptions) and mass spectroscopy (all the synthesized compounds have a very poor solubility in common NMR solvents, even at temperatures of about 80°C).

Liquid crystalline properties

Investigation of the mesomorphic properties of compounds **4a-f** and **5a-g** by POM and DSC evidenced for all the compounds the presence of liquid crystalline properties. The present study focuses on two types of Schiff bases, depending on the nature of the etheric or esteric functional group of the terminal chain. It should be noted that while the Schiff bases containing etheric ending groups have distinct isotropization temperatures, while the Schiff bases containing esteric ending groups decompose above 320°C and therefore the mesophase could be observed only on heating. Considering the low stability of Schiff bases, thermogravimetric studies were carried out. These studies evidenced a very good thermal stability for all the compounds **4a-f**, which were stable at the isotropization

temperature, while compounds **5a-g** decomposed before isotropization.

Table 1 presents the temperatures of the phase transitions determined by using differential scanning calorimetry and/or POM. Classical textures observed by polarized optical microscopy and the low value of thermal effects at liquid crystal/isotropization transitions have demonstrated the presence of nematic mesophases.

The DSC curves revealed polymorphism phenomenon both on heating and cooling cycles, due to reorganization of molecules into solid state. This behavior could be induced by repulsion effects between the hydrogen atom of the azomethinic group and the aromatic system [10].

The behaviors of mesophases for compounds **4a-f** were of enantiotropic type.

The nematic phase of compound **4a** started at 254°C on DSC curves (fig. 1a) and was stable up to 326°C when isotropization occurred. On cooling, the mesophase was stable between 310 and 237°C (when crystallization occurred) and evidenced characteristic nematic droplets (fig. 1b).

The second compound of the series, **4b**, presented a more stable mesophase on heating and cooling stages as well. The analysis in polarized light evidenced a nematic phase that began at 239°C and extended up to 327°C . On cooling the mesophase began at 315°C and kept to 208°C when crystallization occurred.

The increasing of the carbon number in the alkoxy ending groups of compounds **4c** and **4d** induced the increasing of mesophase stability (over 100°C), associated with polymorphism phenomenon. Figure 2a presents the DSC curves for compound **4c** and Figure 2b presents optical texture for compound **4d** on cooling.

On heating, the nematic texture of compound **4e** appeared at 184°C and maintained up to 321°C . On cooling, the nematic mesophase appeared at 309°C (evidenced by POM) and maintained for about 120°C till 184°C (fig. 3).

The increasing of the number of carbon atoms to 18 in compound **4f** decreased the melting point to 172°C and the mesophase stability that isotropized at 280°C (evidenced by POM). This behavior might be caused by the disorder degree induced by longer flexible chain, reported to the length of rigid core. The identified

Compound		K ₁ /K ₂	K ₂ /K ₃	K ₃ /LC ₁	LC ₂ /LC ₃	LC ₂ /I	I/LC ₁	LC ₁ /LC ₂	LC ₂ /K ₁	K ₁ /K ₂
4a	n=6	113	-	-	254	326	310	-	237	-
		[6]	-	-	[-34]	[-13]	[5]	-	[28]	-
4b	n=7	135	203	-	239	327	315*	289	208	-
		[-1]	[-5]	-	[-14]	[-6]	[1]	[13]	-	-
4c	n=8	127	205	-	229	330	318*	305	193	-
		[-16]	[-13]	-	[-31]	[-10]	[2]	[26]	-	-
4d	n=9	138	183	-	219	322	312*	258	176	-
		[-9]	[-4]	-	[-23]	[-4]	[1]	[9]	-	-
4e	n=10	138	-	184	215	321	309*	289	180	-
		[-17]	-	[-0.5]	[-36]	[-4]	[1]	[21]	-	-
4f	n=18	-	-	172	187	280*	275	-	171	150
		-	-	[-1]	[-23]	-	[2]	-	[22]	[6]
5a	n=4	-	228	244	264	333 [^]	-	241	221	-
		-	[-2]	[-6]	[-21]	-	[16]	[1]	-	-
5b	n=5	-	214	232	-	342 [^]	-	223	215	-
		-	[-36]	[-7]	-	-	[2]	[26]	-	-
5c	n=6	80	-	134	-	253 [^]	-	-	-	68
		[-4]	-	[26]	-	-	-	-	[6]	-
5d	n=7	64	-	174	219	343 [^]	-	215	195	67
		[-3]	-	[-0.3]	[-32]	-	[4]	[28]	[2.5]	-
5e	n=8	193	-	204	249	321 [^]	-	237	199	174
		[-5]	-	[-1]	[-13]	-	[7]	[1]	[7]	-
5f	n=9	192	-	204	234	332 [^]	-	224	200	176
		[-7]	-	[-2]	[-7]	-	[6]	[2]	[10]	-
5g	n=17	96	-	194	-	335 [^]	-	184	79	55
		[-22]	-	[-7]	-	-	[6]	[15]	[1]	-

Table 1
TRANSITION TEMPERATURES (°C)
AND TRANSITION ENTHALPIES [KJ/
MOL] FOR COMPOUNDS **4a÷f** AND
5a÷g

Abbreviations: K- crystalline, LC-liquid crystal, I-isotropic

* Data obtained from POM investigations

[^] Data obtained from thermostability study (T_{onset})

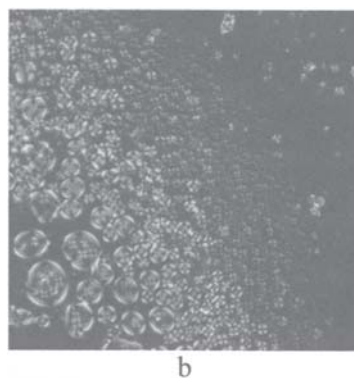
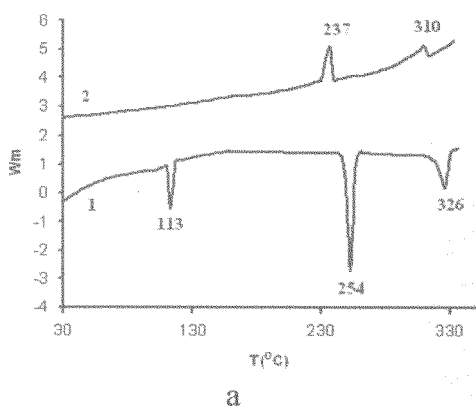


Fig. 1. a) DSC curves of compound **4a**:
1 – first heating; 2 – first cooling;
b) Optical texture of compound **4a**,
275°C, first cooling

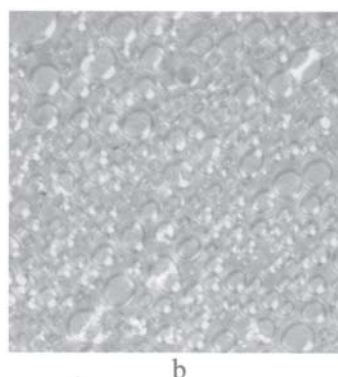
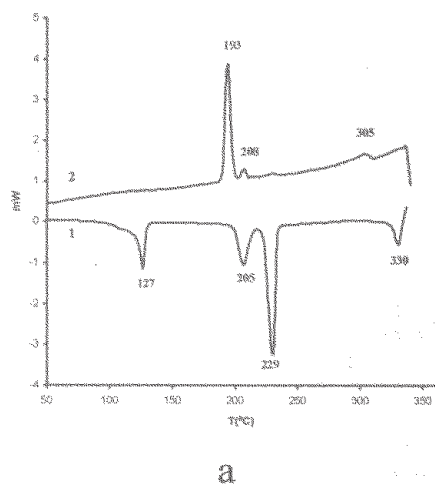


Fig. 2. a) DSC curves of compound **4c**:
1 – first heating; 2 – first cooling;
b) Nematic texture for compound
4d, 252 °C, first cooling

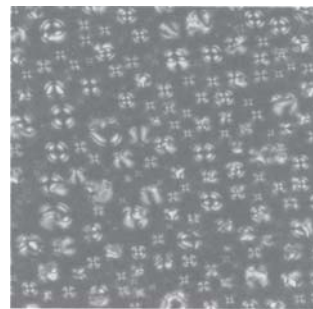
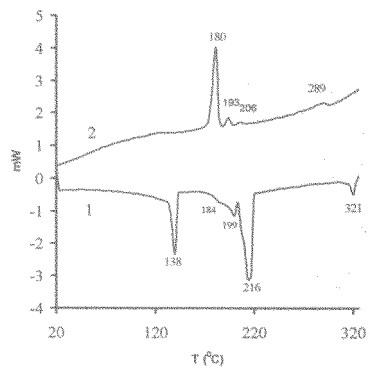


Fig. 3. a) DSC curves of compound **4e**: 1 – first heating; 2 – first cooling;
b) Optical texture of compound **4e**, 184°C, first heating

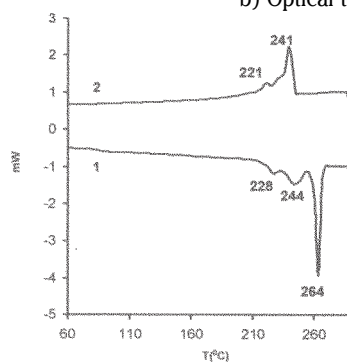


Fig. 4. a) DSC curves of compound **5a**, first heating; 2 – first cooling;
b) Schlieren texture of compound **5a**, 280°C, first heating

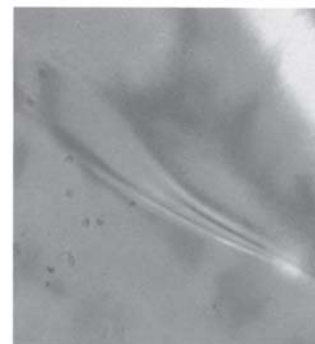
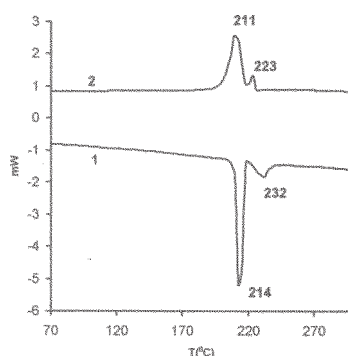


Fig. 5. a) DSC curves of derivative **5b**, first heating; 2 – first cooling;
b) nematic texture of compound **5b**, 317°C, first heating

mesophase observed on optical microscope was similar to derivatives **4 a-e**.

The liquid crystalline/isotropization transitions for the second class of Schiff bases containing an esteric group in the terminal chain (**5a – 5g**) could not be assigned from DSC curves or POM studies because of the degradation processes that begun before isotropization. Therefore, table 1 presents the original temperature values at which degradation started, obtained from TG termogravimetric curves and the DSC were registered only till 280°C (before degradation).

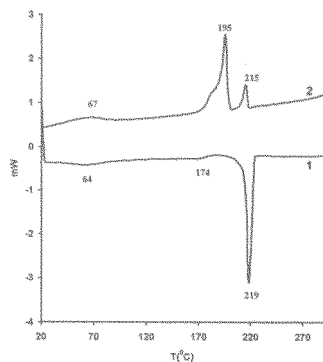
The ordering properties of compound **5a** started on the first heating at 244°C, evidenced on DSC curve as a small transition peak (fig. 4a) that could be associated to a smectic transition, which changed at 264°C into nematic phase with characteristic Schlieren texture (fig. 4b). The nematic phase maintained to 333°C when degradation begun.

The second compound on the series, **5b** presented nematic phase from 232°C to 342°C when degradation occurred. Figure 5b presents the nematic ordering under polarized light at 317°C.

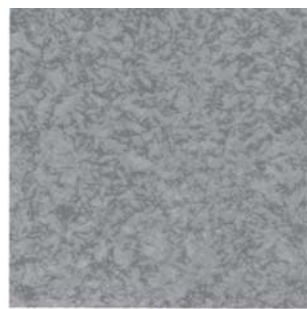
For compounds **5c-g**, a similar polymorphism as for compounds **4a-f** has been observed. Lower isotropization temperature presented compounds **5c** and **5e** (table 1). The mesomorphic properties are of nematic type.

Compound **5d** presents on the DSC curve a very small transition peak at 174°C, corresponding probably to a crystalline-smectic transition, that was stable up to 219°C when changed into a nematic phase (fig.6). It is noteworthy the remarkable stability of the nematic phase, on a 124°C temperature interval (up to 343°C), when decomposition begun.

The largest mesophase interval on heating presented the last compound of the series, **5g**, which melted at 194°C into nematic phase and decomposed at 335°C, so that the



a



b

Fig. 6. a) DSC curves of compound **5d**, first heating; 2 – first cooling;
b) Optical texture of compound **5d**, 200°C, first heating

liquid crystalline properties were maintained for 145°C temperature interval.

Conclusions

This work describes the synthesis and characterization of two new classes of Schiff bases with liquid crystalline properties, based on a 2,5-disubstituted-[1,3,4]oxadiazole bent core and containing azo-aromatic mesogens into structure and alkoxy or alkanoyloxy ending groups. The structure of the compounds has been confirmed by elemental analysis and FT-IR and MS techniques while the mesomorphic properties were assigned by DSC and POM analysis. The liquid crystalline behavior proved at complex the identified mesophases being of nematic or smectic type. Compounds containing terminal alkoxy groups have a much better thermal stability if compared with the alkanoyloxy ones.

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